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(54) Title: HALOGENATED SUPPORTS AND SUPPORTED ACTIVATORS (57) Abstract <p>The present invention is a halogenated support, supported activator and supported transition metal catalyst system involving reacting a carrier containing reactive functionalities with a halogenated organic in the presence of base and contacting a catalytic activator of the formula $[C^+][M^a(Q_1 - Q_{n+1})]$ and/or M^aQ_n a transition metal catalytic precursor with the halogenated support.</p>		

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HALOGENATED SUPPORTS AND SUPPORTED ACTIVATORS**Background of the Invention**

Transition metal catalysts, i.e., Ziegler-Natta and
5 metallocenes, generally cannot be practically used for
gas or slurry phase polymerization unless sufficiently
supported. The use of supported catalysts offers the
possibility of gas and slurry phase compatibility.
Control of the particle size distribution of the
10 polymeric product in the various polymerization processes
eliminates or reduces the extent of reactor fouling.

Supported catalysts for olefin polymerization are
well known in the art. These catalysts offer, among
other things, the advantages of being useable in gas or
15 slurry phase reactors, allowing the control of polymer
particle size and thereby the control of the product bulk
density. Gas phase reactors also eliminate the need for a
solvent and the equipment for solvent handling during
separation of the solvent from the resin. However, it is
20 known that transition metal catalysts, particularly
metallocene catalysts, are deactivated by supports that
contain reactive functionalities, such as silicas which
are oxide supports.

Accordingly, when using supported polyolefin
25 catalysts, it is often desired to remove or reduce
hydroxyl groups and other reactive functionalities from
the support particles before and/or during manufacture of
the supported catalyst. Removal of the reactive
functionalities is often desirable since they will often
30 react with the catalyst thereby deactivating it.

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For example, in the past, various thermal and/or chemical treatments have been used in an effort to achieve dehydroxylation of the oxide particles.

Thermal treatments (i.e., calcining) are
5 advantageous from the point that they do not add undesirable chemicals to the support and that they are relatively simple inexpensive processes. Unfortunately, thermal treatments are often ineffective for achieving a high degree of dehydroxylation. Further, for many porous
10 oxide supports (e.g., silica gel), thermal treatments often result in an undesirable loss of pore volume, shrinkage of the pores and/or loss of surface area.

Furthermore, a variety of chemical treatments have been attempted to remove or deactivate reactive
15 functionalities. Many types of chemicals have been used such as organo aluminum compounds, magnesium chloride/dehydrating agent combinations, organosilanes, halosilanes, silanes, etc. These various chemical processes are often expensive and may result in the
20 addition of undesired or complicating constituents to an oxide support.

Thus, there remains a need for improved catalytic supports and supported activators having the undesired reactive functionalities deactivated.

25 Moreover, it is sometimes desirable to impart different characteristics to the support surface. The attachment of selected organic moieties to the support effects the characteristics of the support and hence the catalytic nature of the catalyst and/or activator placed
30 on the support.

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Thus it is an object of this invention to provide a method to deactivate reactive functionalities on catalytic supports as well to provide for a new support for transition metal catalysts and a supported catalytic activator.

Furthermore, it is an object of the present invention to provide a supported activator and a supported transition metal catalyst and/or catalyst system (support, activator and catalytic precursor) capable of not only producing polymers, but also providing a catalyst with hydrogen sensitivity so as to allow use of hydrogen to control molecular weight in olefin polymerization reactors.

Summary of the Invention

The invention provides supports, supported catalytic activators and supported catalytic systems, wherein the supports have unique surface chemical compositions. The present invention further includes methods for making and using such compositions.

In particular, the present invention uses halogenated organic moieties that are covalently bonded to the support surface. Reactive functionalities on typical catalyst supports, such as hydroxyl groups, known as catalyst poisons, are consumed and the halogenated, most preferably fluorinated, organics are bonded to the support in their stead. These halogenated organic supports are ideal for supporting transition metal catalysts, particularly metallocene and/or Ziegler-Natta catalysts, particularly when a borate and/or aluminate

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catalyst activator is used. The support and supported catalytic activator of the present invention imparts enhanced properties, including improved activity and reduced reactor fouling while obtaining a resin particle of good morphology, bulk density, and enhanced comonomer incorporation.

In one aspect, the present invention is a support composition represented by the following formula.

Carrier - L - RX:,

wherein the Carrier is not particularly limited and includes any material capable of forming a covalent bond to the halogenated organic RX and includes inorganic carriers, inorganic oxide carriers and organic carriers.

Of these, inorganic carriers and inorganic oxide carriers are particularly preferred.

RX is any halogenated organic, wherein X is a halogen group and typically is fluorine, chlorine, iodine, and bromine and mixtures thereof.

L represents the linkage resulting from the reaction of the support reactive functionality with a base (described below) that would be present on the support and capable of forming a covalent bond to the halogenated organic RX.

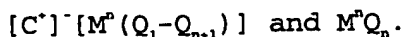
In another aspect of the invention, the invention provides a supported catalytic activator for use with transition metal catalytic precursor represented by the below formula.

Carrier - L - RX::[Compound A]

Where the Carrier, L, and RX are as described above and Compound A is a compound capable of forming an ionic

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complex when reacted with a transition metal catalytic precursor and is further represented by the formulas



[C⁺] is an activating cation, which may be a Bronsted acid capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation; or [C⁺] may be an abstracting moiety that is capable of reacting with a transition metal catalytic precursor resulting in the transition metal cation.

[Mⁿ(Q₁-Q_{n+1})] is a compatible, large (bulky), non-coordinating anion capable of stabilizing the active transition metal catalytic species which is formed when the transition metal catalyst precursor is combined with the supported activator of present invention. These anionic coordination complexes comprise a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid.

Mⁿ(Q_n) is a large (bulky), non-coordinating, neutral species that is capable of stabilizing the active transition metal catalytic species which is formed when the transition metal catalyst precursor is combined with the supported activator of present invention. These anionic coordination complexes comprise a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid.

In a third embodiment of the present invention, the support or the supported activator is combined (in any order of addition) with a transition metal catalytic precursor to provide a supported catalyst or a supported catalytic system. The support or the supported activator

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of the present invention may be combined with the transition metal catalytic precursor either prior to or during introduction to the polymerization reactor zone. Upon contact with the activator, the transition metal precursor reacts to form the active catalytic species.

The invention further includes the method for producing halogenated supports, supported catalytic activators, and catalyst systems as well, and methods for using the halogenated support in transition metal catalyst systems to polymerize olefins, diolefins, cyclic olefins and acetylenically unsaturated monomers to produce polymers, particularly polyethylene.

These and other aspects of the invention will be described in further detail below.

Detailed Description of the Invention

The invention broadly encompasses support particles characterized by the presence of halogenated organic groups on the particle surface represented by the formula Carrier-L-RX;; and further a supported catalytic activator represented by the formula Carrier-L-Rx:: [Compound A] and supported catalyst systems by placing transition metal catalysts on the support of the present invention or the supported catalytic activator of the present invention.

The components of the present invention are described below.

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THE CARRIER

The carrier particles of the invention may be virtually any material having a reactive functionality and capable of forming a covalent bond to the halogenated organic RX.

The carrier suitable for the present invention includes inorganic carriers, inorganic oxide carriers, and organic carriers. Of these, inorganic carriers and inorganic oxide carriers are particularly preferably. More specifically, the inorganic carriers include magnesium compounds or their complex salts such as $MgCl_2$, $MgCl(OEt)$ and $Mg(OEt)_2$, and organic magnesium compounds such as those represent by MgR^aX^b . As used herein, R^a is an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; X^b is a halogen atom; a is a number from 0 to 2 and b is a number from 0 to 2.

Inorganic oxide carriers include talcs, clays, SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 and mixtures thereof such as silica alumina, silica alumina titania, zeolite, ferrite and glass fibers. In addition, the above-mentioned inorganic oxide carriers may contain a small amount of carbonates, nitrates, sulfides or the like.

Additional carrier materials include aluminum phosphate gel materials as well as polymeric or organic supports containing reactive functionalities such as polyvinylchloride, polyvinylalcohol, poly(methylmethacrylate) and hydroxy substituted polystyrene and mixtures of two or more of the foregoing.

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Preferred carrier materials are silica or alumina based materials such as silica, and oxides of Si-Al, Si-Ti, Si-Al-Ti, SiMgCl₂, and aluminum phosphate gel materials and mixtures thereof; and most preferred materials are silica, silica-alumina, silica-alumina-titania and SiMgCl₂, materials and mixtures thereof.

The carriers suitable for this invention can be, but need not be calcined before use.

Preferably, the carriers are compositions conventionally used as a catalyst support material. The degree of porosity in the carrier may be any level that is achievable in the starting material. Preferably, the carrier particles of the present invention have a pore volume of at least 0.3 cc/g; preferably from 0.3 to 5 cc/g; more preferably from 0.3 to 3 cc/g; and most preferably, the pore volume exceeds 1 cc/g. Preferably, the carrier particles have a surface area of about 1-1000 m²/g; preferably from 200 - 800 m²/g; and most preferably from 250 to 650 m²/g. The typical median particle size for a suitable carrier for this invention is from 1 to 300 microns, preferably from 10 to 200 microns, more preferably from 20 to 100 microns.

Pore volume and surface area can be, for example, measured from volume of nitrogen gas adsorbed in accordance with BET method. (Refer to "J. Am. chem. Soc., vol. 60, p. 309 (1983)).

THE LINKER

L represents the linkage resulting from the reaction of the support reactive functionality with a base

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(described below) and is preferably selected from the group comprising oxygen, carbon, sulfur, nitrogen, boron and mixtures thereof, that would be present on the support and capable of forming a covalent bond to the halogenated organic RX.

THE HALOGENATED ORGANIC

The halogenated organic groups on the support particle surface are believed to be substituted for at least some of the reactive functionality groups on the surface of the carrier particles. The net effect of the substitution is to form a linkage (L) between the support and the halogenated organic group (RX) where L and RX is as herein defined. The total amount of RX groups on the support surface is dependent on the number of reactive groups present on the carrier to be treated. The amount of RX groups is typically about 10 mmol per gram of support (mmole/g) or less (but greater than zero), preferably, from 0.1 to 5 mmole/g; and most preferably, from 1.0 to 3.0 mmole/g.

RX is any halogenated organic where X is a halogen group element and is typically fluorine, chlorine, and bromine and mixtures thereof; preferred halogens are fluorine, chlorine, iodine and mixtures thereof; and most preferred is fluorine; and R is mono or multi-cyclic aryls, alkyls, and alkenyl groups and mixtures thereof; preferred are C1-20 alkenyl groups (such as ethene, propylene, butene, and pentene); C1-20 alkyl groups (such as a methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl groups), C6-20 aryl group

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(including substituted aryls) (such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups) and mixtures thereof. More preferred R groups are C1-5 alkyls, C2-5 alkenyls phenyl and naphthyl and mixtures thereof.

Preferred RX compounds are C1-20 halogenated hydrocarbon groups such as XCH_2 , X_2CH , X_3C , $C_2X_nH_{n-5}$ (where $n = 1-5$), $C_3H_nX_{n-7}$ ($n = 1-7$) and $C_6X_nH_{n-6}$ ($n = 1-6$) and mixtures thereof; most preferably, FCH_2 , CHF_2 , F_3C , and fluorosubstituted phenyl, wherein the phenyl can be mono to pentasubstituted (such as p-fluorophenyl, 3,5-difluorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl, and 3,5-bis(trifluoromethyl)phenyl groups) and mixtures thereof; of these the most preferred is pentafluorophenyl.

COMPOUND A

Compound A is a compound capable of forming an ionic complex when reacted with a transition metal catalytic precursor and is further represented by the formulae: $[C^+][M^a(Q_1-Q_{n-1})]$ and $M^a(Q_n)$.

$[C^+]$ is an activating cation, which may be a Bronsted acid capable of donating a proton to the transition metal ionic catalytic precursor resulting in a transition metal cation. Such Bronsted acids include but are not limited to ammoniums, oxoniums, phosphoniums and mixtures thereof; preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-

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dimethylaniline, methyldiphenylamine, pyridine, p-bromo-N,N,-dimethylaniline, p-nitro-N,N-dimethylaniline; phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine; oxoniums from ethers such as diethyl ether, tetrahydrofuran and dioxane; sulfoniums from thioethers such as diethyl thioethers and tetrahydrothiophene; mixtures thereof; most preferably dimethylanilinium.

Furthermore, [C^{*}] may be an abstracting moiety that is capable of reacting with a transition metal catalytic precursor resulting in the transition metal cation. Acceptable abstracting moiety include but are not limited to silver, carbocations, tropylium, carbeniums, ferroceniums and mixtures thereof; preferably carboniums and ferroceniums and mixtures thereof; and most preferably triphenyl carbenium. The [C^{*}] may also include mixtures of the Bronsted acids and the abstracting moiety species.

[M] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state. Preferably, the [M] is boron, aluminum and mixtures thereof.

[Q₁-Q_{n+1}] are independent, wherein Q₁-Q_{n+1} are RX as is defined above and wherein each of the Q in the coordinating anion may be the same or different and may be the same or different from the RX bonded to the support through the linker L defined above. Moreover, in this RX, the Q₁ to Q_n may be hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, substituted hydrocarbyl radicals, halocarbyl

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and substituted-halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted organometalloid radicals. Additionally, the Q_1 to Q_n can simply be the X alone; for example as in BX_n .

5 In addition, neutral $M^n(Q_n)$ can be used in place of the $[C']^-[M^n(Q_1-Q_{n-1})]$, for example $B(C_6F_5)_3$.

Preferred $[M^n(Q_1-Q_{n-1})]$ are selected from the group consisting of BPhenyl_4 , $\text{B}(C_6H_2(CF_3))_4$, $\text{B}(C_6H_5)_4$, AlPhenyl_4 , $\text{Al}(C_6H_2(CF_3))_4$, $\text{Al}(C_6H_5)_4$, PF_6 , BF_4 , B(OPh)_4 and mixtures thereof; preferably $\text{B}(C_6F_5)_4$, $\text{Al}(C_6F_5)_4$, $\text{Al}(C_6H_2(CF_3))_4$, $\text{Al}(C_6H_5)_4$, $\text{BC}_6H_2(CF_3)_4$ and mixtures thereof; most preferred are $\text{B}(C_6F_5)_4$, $\text{Al}(C_6F_5)_4$ and mixtures thereof. Preferred $M^n(Q_n)$ from the neutral species of the preferred list above of $[M^n(Q_1-Q_{n-1})]$.

15 TRANSITION METAL CATALYTIC PRECURSORS

The transition metal catalytic precursors are typically Ziegler-Natta catalysts including metallocenes. The term metallocene is defined as organometallic compounds having a transition metal, including rare earth metals, in coordination with members of at least one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition or rare earth metals.

25 The ansa bridge can be selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as, R^3_2C , R^3_2Si , R^3_2Ge , $R^3_2CR^3_2C$, $R^3_2SiR^3_2Si$, $R^3_2GeR^3_2Ge$, $R^3_2CR^3_2Si$, $R^3_2CR^3_2Ge$, $R^3_2CR^3_2CR^3_2C$, $R^3_2SiR^3_2Si$ diradicals where R^3 is independently selected

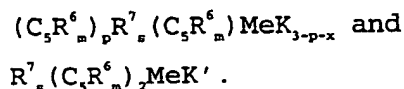
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from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals including ethylene and propylene, Me_2Si (dimethylsilyl), Ph_2Si (diphenylsilyl), Me_2C (isopropylidene), Ph_2P (diphenylphosphoryl) $\text{Me}_2\text{SiSiMe}_2$ (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene, diphenysilyl, dimethylsilyl, propylidene and methylphenylsilyl.

The transition metal component of the metallocene is selected from Groups 3 through 10, lanthanides and actinides of the Periodic Table and mixtures thereof; and most preferably, titanium, zirconium, hafnium, chromium, vanadium, samarium and neodymium and mixtures thereof. Of these Ti, Zr, and Hf and mixtures thereof are most preferable.

In one preferred embodiment, the metallocene catalyst precursor is represented by the general formula $(\text{Cp})_m \text{MR}^4_p \text{R}^5_n$, wherein Cp is a substituted or unsubstituted cyclopentadienyl ring, M is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures thereof; R^4 and R^5 are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; $m=1-3$, $p=0-3$ and the sum of $m+n+p$ equals the oxidation state of M.

In another embodiment the metallocene catalyst is represented by the formulae:



Wherein Me is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures

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thereof; C_5R^6 is a substituted cyclopentadienyl each R^6 , which can be the same or different is hydrogen, alkenyl, aryl, or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms joined together to form a part of a C4 to C6 ring; R^7 is one or more of or a combination of a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical substitution on and bridging two C_5R^6 rings or bridging one C_5R^6 ring back to Me, when $p=0$ and $x=1$ otherwise x is always equal to 0, each K which can be the same or different is an aryl alkyl, alkenyl, alkaryl, or arylalkyl radical having from 1-20 carbon atoms or halogen, K' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 to 1 and when s is 0, m is 5 and p is 0, 1, or 2 and when s is 1, m is 4 and p is 1.

In particular, preferred metallocenes are derivatives of a cyclopentadiene (Cp), including cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, and 1,1-disubstituted silacyclopentadienes, phosphocyclopentadienes, 1-metallocyclopenta-2,4-dienes, bis(indenyl)ethane and mixtures thereof.

Additional illustrative but non-limiting examples of metallocenes represented by the above definition are dialkyl metallocenes such as bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl, bis(cyclopentadienyl)titanium dineopentyl,

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bis(cyclopentadienyl)zirconium di neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide; the trialkyl metallocenes such as cyclopentadienyl titanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienyl zirconium trimethyl, cyclopentadienyl hafnium triphenyl, cyclopentadienyl hafnium trineopentyl, and cyclopentadienyl hafnium trimethyl; monocyclopentadienyls titanocenes such as, pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH₂ and derivatives of this reagent; substituted bis(cyclopentadienyl)titanium (IV) compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, tri-alkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride; silicon, phosphine, amine or carbon bridged

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cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine

dicyclopentadienyl titanium diphenyl or dichloride,

5 methylenedicyclopentadienyl titanium diphenyl or dichloride and other dihalide complexes, and the like; as well as

bridged metallocene compounds such as isopropyl(cyclopentadienyl)(fluorenyl)zirconium dichloride, isopropyl(cyclopentadienyl)(octahydrofluorenyl)zirconium dichloride
10 diphenylmethene(cyclopentadienyl)(fluorenyl) zirconium dichloride, diisopropylmethene(cyclopentadienyl)(fluorenyl)zirconium dichloride, diisobutylmethene(cyclopentadienyl)(fluorenyl) zirconium

15 dichloride, ditertbutylmethene (cyclopentadienyl)(fluorenyl)zirconium dichloride, cyclohexylidene(cyclopentadienyl)(fluorenyl) zirconium dichloride, diisopropylmethene (2,5-

dimethylcyclopentadienyl)(fluorenyl)zirconium
20 dichloride, isopropyl(cyclopentadienyl)(fluorenyl) hafnium dichloride, diphenylmethene (cyclopentadienyl) (fluorenyl)hafnium dichloride, diisopropylmethene(cyclopentadienyl) (fluorenyl)hafnium dichloride, diisobutylmethene(cyclopentadienyl) (fluorenyl)hafnium dichloride,

25 ditertbutylmethene(cyclopentadienyl) (fluorenyl)hafnium dichloride, cyclohexylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride, diisopropylmethene(2,5-dimethylcyclopentadienyl) (fluorenyl)hafnium

dichloride, isopropyl(cyclopentadienyl)(fluorenyl)titanium
30 dichloride, diphenylmethene(cyclopentadienyl)

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(fluorenyl)titanium dichloride, diisopropylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, diisobutylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, ditertbutylmethylene(cyclopentadienyl) (fluorenyl)titanium dichloride, cyclohexylidene(cyclopentadienyl) (fluorenyl)titanium dichloride, diisopropylmethylene(2,5 fluorenyl)titanium dichloride, racemic-ethylene bis (1-indenyl) zirconium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV), dichloride, ethylidene (1-indenyl tetramethylcyclopentadienyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (2-methyl-4-t-butyl-1-cyclopentadienyl) zirconium (IV) dichloride, racemic-ethylene bis (1-indenyl) hafnium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) hafnium (IV) dichloride, racemic-dimethylsilyl (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) hafnium(IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV), dichloride, ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-

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cyclopentadienyl) hafnium (IV) dichloride, racemic-ethylene bis (1-indenyl) titanium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) titanium (IV) dichloride racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, and ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) titanium (IV) dichloride.

Preferred metallocenes are bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)zirconium, isopropyl(cyclopentadienyl)fluorenyl)zirconium dimethyl, bis (1-indenyl) zirconium (IV) dimethyl, (4,5,6,7-tetrahydro-1-indenyl)hafnium(IV)dimethyl, dimethylzirconene, dimethylethylenebisindenylzirconium, and dimethylethylene bis(tetrahydroindenyl)zirconium.

The transition metal catalyst useful in this invention can also include non-cyclopentadienyl catalyst components (such as pentadienyls) as well as ligands such as borollides or carbollides in combination with a transition metal.

Transition metal catalyst precursor also includes traditional Ziegler-Natta ("ZN") catalysts precursor which are represented by the formula M'^aR_n wherein M' is a transitional metal from the Groups 3 through 10, the lanthanide, actinide Series in the Periodic Table, wherein "a" is its valence state and the number of R's is

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equal to "a" and each may be the same or different and independently selected from the group consisting of halogens (preferably Cl and Br); alkyls (preferably C1-C20; more preferably ethyl, butyl, octyl and ethylhexyl);
5 alkoxy (preferably C1-C20, more preferably ethoxy, isopropoxy, butoxy and phenoxy); aryls (preferably C6-C20, including substituted aryls, more preferably phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl
10 groups) and mixtures thereof. For example, TiCl₄, TiCl₃, VOCl₃, VCl₃, TiPhenyl, V(OButyl), tetramethyl zirconium, tetrabenzylzirconium, tetramethoxyzirconium, tetraethoxyzirconium, tetrabutoxyzirconium, bis(2,5-di-t-butylphenoxy)dimethylzirconium, bis(2,5-di-t-butylphenoxy)dichlorozirconium and zirconium
15 bis(acetylacetonate), tetramethyl titanium, tetrabenzyltitanium, tetramethoxytitanium, tetraethoxytitanium, tetrabutoxytitanium, bis(2,5-di-t-butylphenoxy)dimethyltitanium, bis(2,5-di-t-butylphenoxy)dichlorotitanium and titanium
20 bis(acetylacetonate) and mixtures thereof.

METHODS OF PRODUCING THE COMPOSITIONS OF THE PRESENT INVENTION

25 MAKING THE SUPPORT

The methods of the invention generally encompass a step where reactive functionality containing carrier particles are reacted with a halogenated organic in the presence of a base whereby at least a portion of the
30 reactive functionality groups are removed or eliminated

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and the halogenated organic groups are covalently bonded to the carrier particle surface.

The base reactant used is typically a metal hydroxide (such as NaOH or KOH), primary, secondary or tertiary amines (such as methylamine, dimethylamine, triethylamine, dimethylaniline and tributylamine), metal alkyls (wherein the metal is from Group 1, 2, 13, and 14 of the Periodic Table and the alkyl are C1-C8, including n-Butyllithium, dibutyl magnesium, trimethylaluminum, methylaluminum, dimethylaluminum, triethylaluminum, and butyllithium). Preferred bases are NaOH, n-butyllithium, dibutyl magnesium, triethyl amine and tributyl amine. Most preferred bases are NaOH, n-butyllithium, and tributylamine and mixtures thereof.

When an aqueous basic solution is used, the resultant reaction product should have excess water removed.

The methods preferably involve formation of an initial mixture containing the carrier particles, a base and the halogenated organic. The initial mixture preferably also contains a solvent (preferably non-aqueous); however, neat mixtures of the carrier particles, halogen and base may be used. The ingredients forming the initial mixture may be combined in virtually any desired sequence to effect the desired transformation.

While the carrier particles may contain some free water, it is preferred that any free water be removed before the initial mixture is formed. For example, by solvent exchange, heating, and chemical reaction.

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The carrier particles are preferably porous. The porosity of the particles is preferably dictated by the intended end use of the particles. Preferably, the porosity of the particles to be deactivated is such that the resulting particles would be suitable for use as polyolefin catalyst supports.

The initial mixture preferably contains a solvent to facilitate intimate mixing of the carrier particles and the reagents.

The solvent is preferably a non-aqueous solvent. Organic solvents such as C5-C10 hydrocarbons, typically, hexane, tetrahydrofuran, toluene, ether and heptane are generally preferred. The amount of solvent used is not critical, but amounts in excess of that needed to form a pourable slurry are generally unnecessary.

The mixing temperature depends on the solvent and base used and can vary from well below 0°C to the reflux temperature of the solvent, preferably from about 0°C to the reflux temperature of the solvent.

In general the method of the present invention comprises the steps of combining the carrier and the base and mixing a temperature in the range of from about -78°C to the reflux temperature of the solvent (preferably from about 0°C to the reflux temperature of the solvent). The mixing time depends on the mixing temperature. In general the higher the temperature the shorter the time required. Mixing should continue until the reaction between the carrier's functionality groups and the basic reagent is completed.

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While reacting the support with the halogenated organic can generally be completed in a single reaction step, it is possible to repeat the reaction step by recovering the support particles and forming a new reaction mixture in the same manner as for the formation of the initial mixture.

Once the desired level of functionality has been accomplished, the support particles may be recovered from the mixture. The preferred level of the functionality is a approximately 10 mmoles per gram of support; more preferably, 0.1-5 mmole/g; and more preferably, 1-3 mmole/g. This can be determined by known analytical techniques, such as IR, NMR, and elemental analysis.

Preferably, recovery can be accomplished by simply evaporating the solvent and other reactants. In some instances, it may be desirable to wash the halogenated carrier with a solvent to further remove any residual reactants (such as the base), etc. Preferably, however, the reactants are selected such that they are all removable by volatilization. Preferably, the removal is conducted under at least a partial vacuum. If desired, techniques such as spray drying may be employed.

The carrier of the present invention will typically be in the form of a free flowing powder having the surface groups R as defined above used in the reacting step. The recovered product may be further treated as desired to place a catalyst or other constituents on its surface.

This support may be used to support a transition metal catalytic precursor or can be used in another

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embodiment of the present invention to prepare the supported activator.

MAKING THE SUPPORTED ACTIVATOR

5 The activator $[C']^-[M^n(Q_1 - Q_{n-1})]$ and/or $M^n(Q_n)$ as defined above, is dissolved in the desired solvent described above, preferably toluene, C_3 - C_{10} hydrocarbons, and combined with the halogenated support to form a slurry. The reagents are mixed thoroughly using well
10 known mixing and agitation techniques and can be mixed at any appropriate temperature depending on the reagents selected, preferably room temperature. This step can be performed after the halogenated support is prepared or can be accomplished simultaneously with the preparation
15 of the halogenated support by combining all the ingredients in one step.

 These materials can be combined at any temperature suitable for the reagents, typically from about -78°C to the reflux temperature of the halogenated reagent,
20 preferably from about 0°C to the reflux temperature of the solvent. This can be accomplished using multiple mixing steps. For example, the mixing can take place for one period of time at one temperature, e.g., -78°C for two hours and then for another period of time at another
25 temperature, e.g., reflux temperature for two hours. This stepwise (varying time and temperature) can be used for any number of mixing conditions. The time for mixing is dependent on the mixing temperature. In general, it is best to keep the temperature low so as to avoid

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decomposing temperature sensitive reagents. The protocol is selected so as to maximize the efficiency of the reaction.

Once the desired level of activator on the support is achieved the supported activator can be recovered by any of number of usual methods, typically by evaporating the solvent and other reactants.

MAKING THE SUPPORTED CATALYTIC SYSTEMS

Transition metal (Ziegler Natta and/or metallocene) catalyst precursors can be placed on the support and/or supported activator of the present invention through various techniques. For example, once the halogenated support and/or supported activator is prepared, the catalytic precursor can be placed on the support through known techniques such as in a slurry, dry mixing or fluidized gas mixing well known to those skilled in the art. Moreover, an admixture of all necessary reagents can be prepared where the halogenated support, support activator and catalyst system are prepared simultaneously.

Furthermore, the supported activator and catalyst precursor need not be combined until introduced into the polymer reactor zone either before or during the introduction of the monomer feedstock.

METHODS OF USING THE COMPOSITIONS OF THE PRESENT INVENTION

Activation of the supported catalyst or catalytic system of the present invention may be accomplished by

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any suitable method for bringing the support and/or the supported activator into contact with the transition metal catalytic precursor to create the active catalytic species. Such mixing techniques include the mixing of the dry powders, mixing through gaseous impregnation or via a slurry composition in a solvent.

It is also possible to use any of the traditional transition metal catalytic activator co-catalysts which should be selected based on the catalytic system design and desired polymer characteristics.

The activated catalyst is useful to polymerize olefinic materials, particularly ethylene. Polymerizations of olefinic monomers can be accomplished by any number of well known techniques by having the olefinic material come into contact with the polymerization catalyst(s) in a reaction zone under appropriate conditions.

As used herein, "Polymerization" includes copolymerization and terpolymerization and the terms olefins and olefinic monomer includes olefins, alpha-olefins, diolefins, strained cyclic, styrenic monomers, acetylenically unsaturated monomers, cyclic olefins alone or in combination with other unsaturated monomers. While the catalyst system of the present invention is active for this broad range of olefinic monomer feedstock, alpha-olefins polymerizations is preferred, especially the homopolymerization of ethylene or the copolymerization of ethylene with olefins having 3 to 10 carbon atoms.

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"Polymerization techniques" for olefin polymerization according to the present invention can be solution polymerization, slurry polymerization or gas phase polymerization techniques. Method and apparatus for effecting such polymerization reactions are well known and described in, for example, Encyclopedia of Polymer Science and Engineering published by John Wiley and Sons, 1987, Volume 7, pages 480-488 and 1988, Volume 12, pages 504-541. The catalyst according to the present invention can be used in similar amounts and under similar conditions to known olefin polymerization catalyst.

Typically, for the slurry process, the temperature is from approximately 0 degrees C to just below the temperature at which the polymer becomes swollen in the polymerization medium. For the gas phase process, the temperature is from approximately 0 degrees C to just below the melting point of the polymer. For the solution process, the temperature is typically the temperature from which the polymer is soluble in the reaction medium up to approximately 320 degrees C.

The pressure used can be selected from a relatively wide range of suitable pressures, e.g., from subatmospheric to about 350 Mpa. Suitably, the pressure is from atmospheric to about 6.9 Mpa, or 0.05-10 MPa, especially 0.14-5.5 Mpa. Pressure is dictated by the process and the desired product. In the slurry or particle form process, the process is suitably performed with a liquid inert diluent such as a saturated aliphatic hydrocarbon. Suitably the hydrocarbon is a C₄ to C₁₀.

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hydrocarbon, e.g., isobutane or an aromatic hydrocarbon liquid such as benzene, toluene or xylene. The polymer is recovered directly from the gas phase process or by filtration or evaporation from the slurry process or
5 evaporation from the solution process.

The catalysts of the present invention are particularly suited for the gas phase or slurry process.

In addition to the examples of the present invention provided in the Examples 1-17, preferred supports,
10 supported activators, and supported catalyst systems can be prepared from the following materials.

Table of Preferred Materials

Abbreviations:

- 5 TS = Tosyl (paratoluene sulfonic acid)
 APS = aminopropyl silica
 DMAH][BF₂₀] = dimethylanilinium
 tetrakis(pentafluorophenyl)borate
 BEM = butylethylmagnesium;
 10 PVC = Poly(vinylchloride);
 PVA = Poly(vinylalcohol)
 BF₁₅ = tris(pentafluorophenyl)borane;
 TEAL = triethylaluminum;
 TNOA = Tri-n-octylaluminum;
 15 en(ind)₂ = bisindenylethane;
 APG = Aluminumphosphate gel;
 CPS = chloropropyl silica;
 PMMA = Poly(methylmethacrylate);
 CMPS = chloromethylated poly(styrene)
 20 BuCp = butylcyclopentadienyl
 iPr = isopropyl

Carrier	Base/RX	Compound A	Metal Compd.
Silica-200°C	KOH/BrC ₃ F ₇	[DMAH][BF ₂₀]	en(ind) ₂ ZrMe ₂
Silica-400°C	MeOLi/TsOC ₆ F ₅	[DMAH][AlF ₂₀]	en(ind) ₂ HfMe ₂
Silica-600°C	Bu ₂ Mg/ClC ₆ F ₅	TNOA	(BuCp) ₂ ZrCl ₂
Silica-Alumina	MeLi/BrC ₆ F ₅	[DMAH][BF ₂₀]	iPrCpFluZrMe ₂

600°C			
PVC	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	iPrCpFluZrMe ₂
PVC	Bu ₂ Mg/ClC ₆ F ₅	TEAL	(BuCp) ₂ ZrCl ₂
PVA	KOH / (CF ₃) ₂ C ₆ H 3	BF ₁₅	Ph ₂ C (CpTMS) ₂ ZrMe ₂
Silica- Titania 600°C	BEM/ClC ₃ F ₇	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
Silica-600°C	MeLi/Br ₂ C ₆ F ₄	1) t-BuLi 2) BF ₁₅	en(ind) ₂ ZrMe ₂
Silica-600°C	LiAlH ₄ /BrC ₆ F ₅	[Ph ₃ C] [BF ₂₀]	Me ₂ Si (C ₅ Me ₄)N-t- BuZrMe ₂
PVC	MeLi/Br ₂ C ₆ F ₄	B((CF ₃) ₂ C ₆ H ₃) 3	(BuCp) ₂ ZrCl ₂
Silica-800°C	nBuLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	en(ind) ₂ ZrMe ₂
Alumina	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	en(ind) ₂ HfMe ₂
Titania	MeMgCl/BrC ₆ F ₅	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
APG	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	iPrCpFluZrMe ₂
Silica- Titania- Chromia	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	iPrCpFluZrMe ₂
APG	MeNa/BrC ₆ F ₅	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
Silica- Alumina	MeK/BrC ₆ F ₅	[DMAH] [BF ₂₀]	Ph ₂ C (CpTMS) ₂ ZrMe ₂
PVA	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
PVC	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	en(ind) ₂ ZrMe ₂

CMPS	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	Me ₂ Si (C ₅ Me ₄) N-t-BuZrMe ₂
Brominated PE	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
Alumina	MeLi/Br ₂ C ₆ F ₄	1) t- BuLi 2) B((CF ₃) ₂ C ₆ H ₃) 3	(BuCp) ₂ ZrCl ₂
Silica-800°C	Cp ₂ Mg/BrC ₆ F ₅	[DMAH] [BF ₂₀]	Zr(CH ₂ Ph) ₄
Silica-800°C	Bu ₂ Mg/ClC ₆ F ₅	TEAL	TiCl ₄ / (BuCp) ₂ ZrCl ₂
Silica-Titania	Bu ₂ Mg/ClC ₆ F ₅	TNOA	TiCl ₄ / (BuCp) ₂ ZrCl ₂
Silica-600°C	n-BuLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	Ti(CH ₂ Ph) ₄ /Cp ₂ ZrCl ₂
APG	MeOLi/TsOC ₆ F ₅	[DMAH] [AlF ₂₀]	Me ₂ Si (C ₅ Me ₄) N-t-BuZrMe ₂
Silica-Alumina	Bu ₂ Mg/ClC ₆ F ₅	TNOA	(BuCp) ₂ ZrCl ₂
PVA	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
PVC	MeLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	(BuCp) ₂ ZrCl ₂
CMPS	Bu ₂ Mg/ClC ₆ F ₅	TEAL	Zr(CH ₂ Ph) ₄
Brominated PE	KOH/ (CF ₃) ₂ C ₆ H ₃ 3	BF ₁₅	TiCl ₄ / (BuCp) ₂ ZrCl ₂
Alumina	BEM/ClC ₃ F ₇	[DMAH] [BF ₂₀]	TiCl ₄ / (BuCp) ₂ ZrCl ₂
Talc	n-BuLi/BrC ₆ F ₅	[DMAH] [BF ₂₀]	Ti(CH ₂ Ph) ₄ /Cp ₂ ZrCl ₂
Montmorollinite, Clay	MeOLi/TsOC ₆ F ₅	[DMAH] [AlF ₂₀]	Me ₂ Si (C ₅ Me ₄) N-t-BuZrMe ₂

PMMA	Bu ₂ Mg/ClC ₆ F ₅	TNOA	(BuCp) ₂ ZrCl ₂
Talc	MeLi/BrC ₆ F ₅	[DMAH][BF ₂₀]	(BuCp) ₂ ZrCl ₂
Starch	MeLi/BrC ₆ F ₅	[DMAH][BF ₂₀]	(BuCp) ₂ ZrCl ₂
Zeolite	MeLi/BrC ₆ F ₅	[DMAH][AlF ₂₀]	Ti(CH ₂ Ph) ₄ /Cp ₂ ZrCl ₂
CPS	Bu ₂ Mg/ClC ₆ F ₅	TEAL	en(ind) ₂ ZrMe ₂
APS	MeLi/BrC ₆ F ₅	[DMAH][AlF ₂₀]	en(ind) ₂ HfMe ₂
Chlorinated Silica	Bu ₂ Mg/ClC ₆ F ₅	TNOA	iPrCpFluZrMe ₂
Fluorinated Silica	MeOLi/TsOC ₆ F ₅	[DMAH][AlF ₂₀]	Me ₂ Si(C ₅ Me ₄)N-t- BuZrMe ₂
Silica- Magnesia	Bu ₂ Mg/ClC ₆ F ₅	TNOA	(BuCp) ₂ ZrCl ₂
Silica- Magnesia	MeLi/BrC ₆ F ₅	[DMAH][BF ₂₀]	(BuCp) ₂ ZrCl ₂
Silica-600°C	Bu ₂ Mg/ClC ₆ F ₅	TNOA	TiCl ₄
Silica-600°C	KOH/ Cl ₃ CCO ₂ C ₂ Cl ₇	Al ₂ Et ₃ Cl ₃	VOCl ₃
Silica-600°C	Bu ₂ Mg/ClC ₆ F ₅	TNOA	VOCl ₃ /TiCl ₄
Silica-600°C	MeLi/BrC ₆ F ₅	BF ₁₅ /TEAL	VOCl ₃ /Zr(CH ₂ Ph) ₄

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The invention is further illustrated by the following examples. It is understood that the invention is not limited to the specific details of the examples.

5

Examples 1-14

10

Examples 1-10 are example of modifying a carrier containing reactive functionalities to create the support of the present invention. Examples 11 and 12 are examples of preparing the supported activator according to the present invention. Examples 14 are examples of the supported activator catalyst system according to the present invention.

15

Abbreviations: Si-Al= Silica Alumina

Si-MgCl₂ = Silica Supported Magnesium
Chloride

Si-Al-Ti = Silica Alumina Titania Cogel

CMPS = Chloromethylated Poly(styrene)

H-PS = Poly(4-hydroxystyrene)

20

PVA = Poly(vinylalcohol)

BPFB = Bromopentafluorobenzene

4-BTFT = 4-Bromotetrafluorotoluene

B-3,5-DTFMB = Bromo-3,5-

di(trifluoromethyl)benzene

25

1,4-DBTFB = 1,4-Dibromotetrafluorobenzene

TFMI = Trifluoromethyliodide

EXAMPLES 1-14

EX.	CARRIER	BASE	SOL- VENT	HALO. ORG.	COMMENTS
1	Silica	NaOH	H ₂ O	BPFB	100g of silica is slurried with 0.3 moles of NaOH in 1L of water for 4 hours. The support is filtered, washed and dried. 20g of the support is slurried in 150 mL of hexanes and cooled to -78°C under an atmosphere of argon. 80 mmols of BPFB is added as a hexane solution. The slurry is mixed for 1 hour at -78°C and warmed to room temperature (mixed 4h). The support is filtered and dried in vacuo.
2	Alumina	Bu ₃ N	Hexanes	4-BTFT	100g of alumina is slurried with 0.4 moles of Bu ₃ N in 1L of hexanes for 4 hours. The support is filtered, washed and dried under an atmosphere of argon. 20g of the support is slurried in 150 mL of hexanes and cooled to -78°C under an atmosphere of argon. 80 mmols of 4-BTFT is added as a hexane solution. The slurry is mixed for 1 hour at -78°C and warmed to room temperature (mixed 4h). The support is filtered and dried in vacuo.
3	CMPS	n-BuLi	Hexanes	BPFB	20g of CMPS is slurried with enough n-BuLi in 100mL of hexanes at 0°C and warmed to RT for 4 hours to react

					with all pendant chlorines. The reacted support is cooled to -78°C under an atmosphere of argon. BPFB is added as a hexane solution to react with the produced anionic sites. The slurry is mixed for 1 hour at -78°C and warmed to room temperature (mixed 4h). The support is filtered and dried in vacuo.

EX.	CARRIER	BASE	SOL- VENT	HALO. ORG.	COMMENTS
4	Silica	n-BuLi	Hexanes	B-3,5-DTFMB	100g of silica is slurried with 0.3 moles of n-BuLi in 1L of hexanes at 0°C for 1 hour and RT for 2 hours. The support is filtered, washed and dried. 20g of the support is slurried in 150 mL of hexanes and cooled to -78°C under an atmosphere of argon. 80 mmols of B-3,5-DTFMB is added as a hexane solution. The slurry is mixed for 1 hour at -78°C and warmed to room temperature (mixed 4h). The support is filtered, washed, and dried in vacuo.
5	Silica	KOH	H ₂ O	1,4-DBTFB	100g of silica is slurried with 0.3 moles of KOH in 1L of water for 4 hours. The support is filtered, washed and dried. 20g of the support is slurried in 150 mL of hexanes and cooled to -78°C under an atmosphere of argon. 80 mmols of 1,4-DBTFB is added as a hexane solution. The slurry is mixed for 1 hour at -78°C and warmed to room temperature (mixed

6	Si-Al	MeLi	Ethe r	BPFB	<p>4h). The support is filtered, washed and dried in vacuo.</p> <p>100g of silica-alumina is slurried with 0.3 moles of MeLi in 1L of diethyl ether at 0°C for 2 hours and at RT for 4 hours. The support is filtered, washed and dried. 20g of the support is slurried in 150 mL of hexanes and cooled to -78°C under an atmosphere of argon. 80 mmols of BPFB is added as a hexane solution. The slurry is mixed for 1 hour at -78°C and warmed to room temperature (mixed 4h). The support is washed, filtered and dried in vacuo.</p>
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EX.	CARRIER	BASE	SOLVENT	HALO. ORG.	COMMENTS
7	Si-MgCl ₂	Bu ₂ Mg	Heptanes	BPFB	100g of silica supported magnesium chloride is slurried in 1L of heptanes and cooled to 0°C. 200 mmol of DBM is added as a heptane solution and mixed for 1 hour. The slurry is warmed to RT for 4 hours. The support is filtered, washed and dried in vacuo. 20g of this support is slurried 200mL of hexanes under an argon atmosphere and cooled to -78°C. 80 mmol of BPFB is added as a hexane solution and the reaction media is mixed for 1 hour. After warming to RT the slurry is stirred an additional 4 hours prior to filtering, washing and drying in vacuo.
8	Si-Al-Ti	Bu ₂ Mg	Toluene	BPFB	100g of silica-alumina-titania cogel is slurried in 1L of toluene and cooled to 0°C. 200 mmol of DBM is added as a toluene solution and mixed for 1 hour. The slurry is warmed to RT for 4 hours. The support is filtered, washed and dried in vacuo. 20g of this support is slurried 200mL of

					hexanes under an argon atmosphere and cooled to -78°C. 80 mmol of BPFB is added as a hexane solution and the reaction media is mixed for 1 hour. After warming to RT the slurry is stirred an additional 4 hours prior to filtering, washing and drying in vacuo.
9	H-PS	Bu ₂ Mg	Toluene	BPFB	100g of poly(hydroxystyrene) is swollen in 1L of toluene and cooled to 0°C. DEM is added as a toluene solution to deprotonate the polymer and mixed for 1 hour. The slurry is warmed to RT for 4 hours. The support is filtered, washed and dried in vacuo. 20g of this support is slurried 200mL of toluene under an argon atmosphere and cooled to -78°C. BPFB is added as a toluene solution to react with the formed phenoxide anions and the reaction media is mixed for 1 hour. After warming to RT the slurry is stirred an additional 4 hours prior to filtering, washing and drying in vacuo.
10	PVA	NaAc	H ₂ O	TFMI	100g of poly(vinylalcohol) is dissolved in 1L of water and cooled to 0°C. Sodium acetate is added

[illegible]

EX.	Carrier	Activator	COMMENTS
11	Ex. 5	BF ₁₅	The support is slurried in hexane and cooled to -78°C under an atmosphere of dry, deoxygenated argon. t-Butyllithium is added to debrominate the supported organic moiety. The slurry is warmed to room temperature and a solution of BF ₁₅ is added. The slurry is mixed a further 2 hours and the solid is filtered, washed and dried in vacuo.
12	Ex. 1	[DMAH][BF ₂ O]	The support is slurried in hexanes and [DMAH][BF ₂₀] is added as a solution. After one hour of mixing the solvents are removed in vacuo.
13	Ex. 3	[DMAH][BF ₂ O]	The support is swollen in toluene and [DMAH][BF ₂₀] is added as a solution. After one hour of mixing the solvents are removed in vacuo.
14	Ex. 8	[DMAH][BF ₂ O] Cp ₂ ZrMe ₂	The support is slurried in hexanes and a mixture of [DMAH][BF ₂₀] and Cp ₂ ZrMe ₂ is added as a solution at 0°C. After one hour of mixing the solvents are removed in vacuo.

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POLYMERIZATION EXAMPLEExample 15 -- The Support

SiO₂, available from Grace Davison, a business unit of W.R. Grace Co.-Coon., as Sylopol® 948 (30g, previously calcined at 800°C for 4 hours), was slurried in 150 mL of hexanes under an atmosphere of purified argon and cooled to 0°C. A hexane solution of n-BuLi (80 mmol) was added and mixed for 2 hours at 0°C. After warming to RT, the slurry was mixed an additional 16 hours. The slurry was recooled to 0°C and neat bromopentafluorobenzene (100 mmol) was added. After mixing 1 hour at 0°C, the slurry was warmed to RT and mixed a further 16 hours. The liquid phase was removed and the solids washed with hexanes (3 times with 75 mL). The solid was dried in vacuo.

Example 16 -- The Supported Activator

To Example A (2.4g) was added toluene (50mL) under an atmosphere of dry, deoxygenated argon. A toluene solution of [DMAH][BF₂O] (50mL, 1mmol) was added to the foregoing slurry. The light green slurry was mixed for 1 hour. The liquid phase was removed and the solids washed with hexanes (3 times with 50 mL). The solid was dried in vacuo.

Example 17 -- The Support Catalyst System

A 500 mL polymerization vessel was charged, in order, with heptanes (150 mL), TEAL (1 mmol), Example B (100 mg) and zirconocene dichloride (40 mmol) under an

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atmosphere of dry, deoxygenated argon at 40°C. The
reactor was refilled with ethylene to a pressure of 45
psig after evacuation. Polymerization was carried out
for 30 minutes and was quenched by rapid venting of
5 monomer followed by methanol (50 mL). The polymer was
washed with methanol and dried more than 12 hours in a
vacuum oven at 60°C to yield 15 g of polyethylene.

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WHAT IS CLAIMED IS:

1. A catalyst support composition represented by the following formula

5 Carrier - L - RX:,

wherein the Carrier is selected from the group of inorganic compounds, inorganic oxides, gels, polymeric materials and mixtures thereof having reactive functionalities;

10 L is represents the linkage resulting from the reaction of the support reactive functionality with a base reactant; and

RX is any halogenated organic.

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2. The catalyst support composition of claim 1, wherein the composition further comprises:

the Carrier is a material selected from the group comprising magnesium salts and organic magnesium compounds represent by $MgR^a_aX^b_b$, wherein R^a is an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; X^b is a halogen atom; a is a number from 0 to 2 and b is a number from 0 to 2; inorganic oxides selected from the group of talcs, clays, SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , aluminum phosphate gels; and polyvinylchloride and hydroxy substituted polystyrene and mixtures of two or more of the foregoing;

L is selected from the group comprising oxygen, carbon, sulfur, nitrogen, boron and mixtures thereof; and

RX is a compound wherein X is fluorine, chlorine, and bromine and mixtures thereof and R is mono or multi-cyclic aryl, alkyl, and alkenyl compounds and mixtures thereof.

3. The catalyst support according to claim 2 wherein the R in the RX compound is selected from the group comprising C1-20 alkenyl groups, C1-20 alkyl groups, C6-20 aryl groups and mixtures thereof.

4. The catalyst support according to claim 3 wherein the R in the RX compound is selected from the

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group comprising ethenyl, propenyl, butenyl, and
pentenyl, methyl, ethyl, n-propyl, iso-propyl, n-butyl,
n-octyl, and 2-ethylhexyl groups, a methyl, ethyl, n-
propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl
5 phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-
dimethylphenyl, 3,5-dimethylphenyl, 2,4-dimethylphenyl,
2,3-dimethylphenyl groups and mixtures thereof.

5. The catalyst support according to claim 4
10 wherein the RX is selected from the group comprising FCH_2 ,
 CHF_2 , F_3C , p-fluorophenyl, 3,5-difluorophenyl,
pentafluorophenyl, 3,4,5-trifluorophenyl, and 3,5-
bis(trifluoromethyl)phenyl and mixtures thereof.

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6. A supported catalytic activator composition represented by the formula

Carrier-L-Rx:: [Compound A]

wherein the Carrier is selected from the group of
5 inorganic compounds, inorganic oxides, gels, polymeric materials and mixtures thereof having reactive functionalities;

L represents the linkage resulting from the reaction of the support reactive functionality with a
10 base reactant;

RX is any halogenated organic; and

Compound A is represented by the formulas

$[C^+][M^n(Q_1-Q_{n+1})]$ and $M^n(Q_n)$, wherein

[C] is an activating cation, which may be a Bronsted
15 acid capable of donating a proton to the transition metal ionic catalytic precursor resulting in a transition metal cation or an abstracting moiety that is capable of reacting with a transition metal catalytic precursor resulting in the transition metal cation;

20 [M] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state; and

Q_1-Q_{n+1} may be the same or different and are independently selected and, wherein Q_1-Q_{n+1} are selected
25 from halogens, halogenated organics, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, substituted hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals,

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hydrocarbyl and halocarbyl-substituted organometalloid
radicals and mixtures thereof.

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7. The activator composition of claim 6, wherein the composition further comprises:

the Carrier is a material selected from the group comprising magnesium salts and organic magnesium compounds represent by $MgR^a_aX^b_b$, wherein R^a is an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; X^b is a halogen atom; a is a number from 0 to 2 and b is a number from 0 to 2, inorganic oxides selected from the group of talcs, clays, SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , aluminum phosphate gels; and polyvinylchloride and hydroxy substituted polystyrene and mixtures of two or more of the foregoing;

L is selected from the group comprising oxygen, carbon, sulfur, nitrogen, boron and mixtures thereof;

RX is a compound wherein X is fluorine, chlorine, and bromine and mixtures thereof and R is mono or multi-cyclic aryl, alkyl, and alkenyl compounds and mixtures thereof;

C is selected from the group comprising ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyride, p-bromo-N,N,-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine, oxoniums from ethers, sulfoniums from thioethers, silver, carbocations,

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tropylium, carbeniums, ferroceniums and mixtures thereof;
and

5 Q_1-Q_{n+1} is selected from the group comprising
fluorine, chlorine, and bromine, BPhenyl₄,
B(C₆H₂(CF₃)₃)₄, B(C₆H₅)₄, AlPhenyl₄, Al(C₆H₂(CF₃)₃)₄,
Al(C₆H₅)₄, PF₆, BF₄, B(OPh)₄ and mixtures thereof.

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8. The activator compound of claim 7 wherein the R in the RX compound is selected from the group comprising C1-20 alkenyl groups, C1-20 alkyl groups, C6-20 aryl groups and mixtures thereof.

5

9. The activator of claim 8 wherein the R in the RX compound is selected from the group comprising ethenyl, propenyl, butenyl, and pentenyl, methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl groups, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups and mixtures thereof.

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10. The activator according to claim 9, wherein the RX is selected from the group comprising FCH_3 , CHF_2 , F_3C , p-fluorophenyl, 3,5-difluorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl, and 3,5-bis(trifluoromethyl)phenyl and mixtures thereof.

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11. A supported catalyst system comprising a supported activator represented by the formula Carrier-L-Rx::[Compound A] and a transition metal catalyst precursors, wherein:

5 the Carrier is selected from the group of inorganic compounds, inorganic oxides, gels, polymeric materials and mixtures thereof having reactive functionalities;

L is represents the linkage resulting from the reaction of the support reactive functionality with a
10 base reactant;

RX is any halogenated organic; and

Compound A is represented by the formulas

$[C^+][M^+(Q_1-Q_{n+1})]$ and $M^+(Q_n)$, wherein

[C] is an activating cation, which may be a Bronsted
15 acid capable of donating a proton to the transition metal ionic catalytic precursor resulting in a transition metal cation or an abstracting moiety that is capable of reacting with a transition metal catalytic precursor resulting in the transition metal cation;

20 [M] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state; and

Q_1-Q_{n+1} may be the same or different and are
independently selected and are selected from halogens,
25 halogenated organics, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxide radicals, substituted hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl and

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halocarbyl-substituted organometalloid radicals and mixtures thereof; and the transition metal catalyst precursor is selected from the group comprising Ziegler-Nattas, metallocenes and mixtures thereof.

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12. The catalyst support composition of claim 11 wherein the composition further comprises:

the Carrier is a material selected from the group comprising magnesium salts and organic magnesium compounds represent by $MgR^a_aX^b_b$, wherein R^a is an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; X^b is a halogen atom; a is a number from 0 to 2 and b is a number from 0 to 2; inorganic oxides selected from the group of talcs, clays, SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , aluminum phosphate gels; and polyvinylchloride and hydroxy substituted polystyrene and mixtures of two or more of the foregoing;

L is selected from the group comprising oxygen, carbon, sulfur, nitrogen, boron and mixtures thereof;

RX is a compound wherein X is fluorine, chlorine, and bromine and mixtures thereof and R is mono or multi-cyclic aryl, alkyl, and alkenyl compounds and mixtures thereof;

C is selected from the group comprising ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo-N,N,-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine, oxoniums from

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ethers, sulfoniums from thioethers, silver, carbocations, tropylium, carbeniums, ferroceniums and mixtures thereof;

Q_1-Q_n is fluorine, chlorine, and bromine, halogenated mono or multi-cyclic aryl, alkyl, and alkenyl compounds, BPhenyl₄, B(C₆H₂(CF₃)₃)₄, B(C₆H₃)₄, AlPhenyl₄, Al(C₆H₂(CF₃)₃)₄, Al(C₆H₃)₄, PF₆, BF₄, B(OPhenyl)₄, and mixtures thereof; and

the transition metal catalyst precursor is selected from the group of (1) organometallic compounds having a transition metal in coordination with members of at least one five-member carbon ring, heterosubstituted five member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition metal wherein the transition metal is selected from the Group 3 through 10, lanthanide and actinide metals from the Periodic Table, (2) organometallic compounds represented by the formula M'^aR_a wherein M' is a transitional metal from the Groups 3 through 10 the lanthanide and actinide Series in the Periodic Table, wherein 'a' is its valence state and the number of R's is equal to 'a' and each may be the same or different and independently selected from the group consisting of halogens, alkyls, alkoxys, aryls and mixtures two or more of the foregoing thereof.

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13. The catalyst support composition of claim 12 wherein the composition further comprises:

the Carrier is a material selected from the group comprising magnesium salts and organic magnesium compounds represent by $MgR^a_aX^b_b$, wherein R^a is an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms; X^b is a halogen atom; a is a number from 0 to 2 and b is a number from 0 to 2; inorganic oxides selected from the group of talcs, clays, SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , aluminum phosphate gels; and polyvinylchloride and hydroxy substituted polystyrene and mixtures of two or more of the foregoing;

L is selected from the group comprising oxygen, carbon, sulfur, nitrogen, boron and mixtures thereof;

RX is a compound wherein X is fluorine, chlorine, and bromine and mixtures thereof and R is mono or multi-cyclic aryl, alkyl, and alkenyl compounds and mixtures thereof;

C is selected from the group comprising ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyride, p-bromo-N,N,-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine, oxoniums from

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ethers, sulfoniums from thioethers, silver, carbocations, tropylium, carbeniums, ferroceniums and mixtures thereof;

Q_1-Q_{n-1} is fluorine, chlorine, and bromine, halogenated mono or multi-cyclic aryl, alkyl, and alkenyl compounds, BPhenyl₄, B(C₆H₄(CF₃)₃)₄, B(C₆H₅)₄, AlPhenyl₄, Al(C₆H₄(CF₃)₃)₄, Al(C₆H₅)₄, PF₆, BF₄, B(OPhenyl)₄ and mixtures thereof; and

the transition metal catalyst precursor is selected from the group of comprising (1) metallocenes represented by the formula (Cp)_mMR³_nR⁴_p, wherein Cp is a substituted or unsubstituted cyclopentadienyl ring, M is a Groups 3-6, lanthanide, actinide metals from the Periodic Table and mixtures thereof; R³ and R⁴ are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m=1-3, p= 0-3 and the sum of m+n+p equals the oxidation state of M, and (2) the R⁵ selected from the group consisting of Cl, Br, C1-C20 alkyls, C1-C20 alkoxys, C6-C20 aryls and mixtures thereof.

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14. The catalyst system of claim 12 wherein the R in the RX compound is selected from the group comprising ethenyl, propenyl, butenyl, and pentenyl, methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl groups, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5- methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups and mixture thereof; and

the transition metal compound is selected from the group comprising $TiCl_4$, $TiCl_3$, $VOCl_3$, VCl_3 , $TiPhenyl_4$, $V(OButyl)_3$, tetramethyl zirconium, tetrabenzylzirconium, tetramethoxyzirconium, tetraethoxyzirconium, tetrabutoxyzirconium, bis(2,5-di-t-butylphenoxy)dimethylzirconium, bis(2,5-di-t-butylphenoxy)dichlorozirconium and zirconium bis(acetylacetonate), tetramethyl titanium, tetrabenzyltitanium, tetramethoxytitanium, tetraethoxytitanium, tetrabutoxytitanium, bis(2,5-di-t-butylphenoxy)dimethyltitanium, bis(2,5-di-t-butylphenoxy)dichlorotitanium, titanium bis(acetylacetonate), bis(indenyl)ethanebis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)zirconium-dimethyl, isopropyl(cyclopentadienyl)fluorenyl)zirconium, dimethyl, bis (1-indenyl) zirconium (IV) dimethyl, (4,5,6,7-tetrahydro-1- indenyl)hafnium(IV)dimethyl, dimethylzirconene, dimethyethylenebisindenylzirconium,

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and dimethylethylene bis(tetrahydroindenyl)zirconium and mixtures thereof.

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15. The catalyst system composition according to claim 14, wherein the RX is selected from the group comprising FCH_2 , CHF_2 , F_3C , p-fluorophenyl, 3,5-difluorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl, and 3,5-bis(trifluoromethyl)phenyl groups) and mixtures thereof.

16. The method of making the catalytic support according to claims 1-5, the steps of said method comprising reacting the carrier with the halogenated organic RX in the presence of a base to prepare a halogenated support.

17. The method of claim 16, wherein said method further comprises the steps of using a base selected from the group comprising metal hydroxides, primary, secondary and tertiary amines, metal alkyls and mixtures thereof.

18. The method of claim 17, wherein said method further comprises using a base selected from the group comprising NaOH, n-butyllithium, dibutylmagnesium, triethylamine, tributylamine and mixtures thereof.

19. The method of claim 16, wherein said method further comprises the steps of performing the reaction in a non-aqueous solvent.

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20. The method of claim 19, wherein the method further comprises using a solvent selected from the group comprising hexane, tetrahydrofuran, toluene, ethane, heptane and mixtures thereof.

5

21. The method of making the support activator of claims 6-10, wherein the method comprises the steps of:

- 1) reacting the carrier with the halogenated organic RX in the presence of a base to prepare a
10 halogenated support; and
- 2) contacting the halogenated support from step 1) with the activator Compound A represented by the formulas $[C^+][M^+(Q_1-Q_m)]$ and $M^+(Q_n)$ of claims 6 - 10.

15

22. The method of claim 21, wherein the steps further comprise dissolving the activator Compound A in an organic solvent prior to bring Compound A into contact with the halogenated support from step 1).

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23. The method of claim 22, wherein the steps further comprise using a C5-C10 hydrocarbon to dissolve Compound A.

25

24. The method of claim 21 wherein the steps are performed simultaneously.

25. The method preparing a supported catalyst system of claims 11-15, wherein the method comprising

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contacting the supported activator prepared in accordance with claims 21-24, and with the transition metal catalyst precursor.

5 26. The method of claim 25 wherein the steps are performed simultaneously.

10 27. A process for the production of olefinic polymers which comprises contacting olefinic monomeric materials under polymerization conditions with the catalyst system of claims 11-15.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/US 96/06471

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F4/02 C08F10/00 C08F4/603

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	W0,A,93 11172 (EXXON) 10 June 1993 see claims 1,2,10,13,17,18 see page 37, line 17 - page 38, line 14 see figure 8 ---	1-27
P,X	US,A,5 473 020 (PEIFER BERND) 5 December 1995 see column 10 - column 11; example 2 see claim 1 ---	1,16-20
A	US,A,3 888 789 (DOMBRO ROBERT A.) 10 June 1975 see column 5, line 57 - column 7, line 65 see column 11; example III --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Intern: J Application No
PCT/US 96/06471

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO,A,95 07140 (MOBIL OIL) 16 March 1995 see page 10; example 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 96/06471

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US-A-3888789	10-06-75	NONE	
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